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Effects of UV-dechloramination of swimming pool water on the formation of disinfection by-products: A lab-scale study.

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Abstract

UV dechloramination has become a very popular process for reducing the concentration of chloramines in public swimming pool water. As the effects of this process on the formation of disinfection by-products (DBPs) remain a controversial issue, a bench-scale study has been undertaken to examine the impact of UV dechloramination on the formation of various DBPs. Four pool water samples were exposed to UV radiation at 254 nm in the presence of free chlorine ($[Cl_2]_0$ = 3 mg L^{-1}) and then chlorinated in the dark for 24 h ($[Cl_2]_0$ = 3 mg L^{-1}). High UV doses (up to 47 kJ m^{-2}) were used to simulate cumulative UV doses received by real pool waters. The data showed that UV irradiation led to a 90 % photodecay of free chlorine for UV doses ranging from 13 to 20 kJ m^{-2}, to the formation of chlorate ion (0.05-0.11 mole of chlorate/mole of free chlorine decomposed) and to a significant increase in the chlorine demand of pool water during the post-chlorination step. UV exposure followed by post-chlorination did not significantly affect the formation of haloacetic acids, led to a small increase in the concentrations of adsorbable organic halogen (AOX) and of chloral hydrate and markedly increased the formation of trihalomethanes (chloroform, bromodichloromethane, chlorodibromomethane), dichloroacetonitrile, 1,1,1-trichloropropanone and chloropicrin.

Key-words: Chlorine demand, Trihalomethanes, Chloral hydrate, Haloacetonitriles, Haloacetic acids, 1,1-Dichloropropanone, 1,1,1-Trichloropropanone, Chloropicrin, Chlorate.

Abbreviations used for DBPs

AOX: adsorbable organic halogen

BCAA: bromochloroacetic acid

BCAN: bromochloroacetonitrile

BDCM: bromodichloromethane

CDBM: chlorodibromomethane

CH: chloral hydrate

DBAN: dibromoacetonitrile

DBCAA: dibromochloroacetic acid

DBPs: disinfection by-products

DCAA: dichloroacetic acid

DCAN: dichloroacetonitrile

DCP: 1,1-dichloropropanone

HAAs: haloacetic acids

HANs: haloacetonitriles

MCAA: monochloroacetic acid

TBM: bromoform (tribromomethane)

TCAA: trichloroacetic acid

TCAN: trichloroacetonitrile

TCM: chloroform (trichloromethane)

TCNM: chloropicrin (trichloronitromethane)

TCP: 1,1,1-trichloropropanone

TOC: Total Organic Carbon

THMs: trihalomethanes

TTHMs: total trihalomethanes

1. Introduction

Chlorine gas and sodium or calcium hypochlorite are the most common chemicals used for the disinfection of swimming pool water. According to the French regulations, the concentration of hypochlorous acid (HOCl) in water and the pH must be kept between 0.4 and 1.4 mg Cl_2 L^{-1} and 6.9 and 7.7, respectively [1]. Besides its disinfecting properties, chlorine reacts with contaminants introduced in water by the bathers to produce numerous undesirable disinfection by-products (DBPs), such as inorganic chloramines and organohalogenated by-products [2-8]

Among the inorganic chloramines, it is well-known that trichloramine (NCl_3) is very volatile and is a powerful irritant for eye and for the upper respiratory tract [9]. Exposure to trichloramine and to other volatile DBPs in swimming pool water can damage the lung epithelium of swimmers and may be involved in the asthma rise in children and lifeguards [10-12]. The concentration of trichloramine in the atmosphere of indoor swimming pool is not regulated. However, the French Institute of Occupational Health and Safety (INRS) has recommended a comfort limit value of 0.5 mg NCl_3 m^{-3} [9]. The concentration of combined chlorine in water must not exceed 0.6 mg Cl_2 L^{-1} in French public pools [1]. In order to meet this regulation, more than 500 French public pools have been equipped with a UV reactor during the last decade. Several UV systems equipped with Low Pressure (noted as LPUV) or with Medium Pressure (MPUV) lamps have been approved by the French Ministry of Health for dechloramination purposes [13]. In the pool water treatment chain, the UV reactor is inserted between the sand filter and the on-line injection point of the disinfectant. UV systems are usually operated at UV doses of 600 J m^{-2}. In current applications, UV dechloramination is an efficient process for

decreasing the concentration of combined chlorine because pool water is continuously recirculated through the UV reactor [13]. For a turnover period of pool water of about 1.5 h, the cumulative dose of UV received by water is approximately equal to 10 kJ m^{-2} daily and therefore, the UV treatment will theoretically remove 90 % of trichloramine after one day of treatment (Table S1 in the Supplementary Material). It must also be emphasized that UV dechloramination of swimming pool water will also decompose free chlorine because hypochlorous acid and hypochlorite ion absorb UV light [14]. In pure water, the photodecomposition rate of free chlorine at 254 nm is slower than the rates of photolysis of mono and dichloramine and is significantly faster in the presence of organic solutes [14]. The mechanisms of photodecomposition of chloramines and free chlorine are quite complex and are not well elucidated. Recent works showed that inorganic chloramines are decomposed by UV light into inorganic radicals and nitrite ions as intermediates and into ammonium, nitrite, nitrate and nitrous oxide as stable end-products [15-17]. Free chlorine photolysis leads to the formation of hydroxyl radicals and chlorine atoms as transient species which can further react with free chlorine to produce chloride ions and other oxychlorine species [15, 18-20].

Most of the reactions initiated by UV photolysis of chloramines and free chlorine are currently unknown but these reactions may affect the production of DBPs. To our knowledge, only four full-scale studies on the effects of UV dechloramination on the concentrations of DBPs in swimming pool have been published. The data obtained by Gérardin et al. [21] with reactors equipped with LPUV and MPUV lamps and by Cassan et al. [22] with a reactor equipped with MPUV lamps showed that UV dechloramination may increase the concentrations of trihalomethanes (THMs) in water by up to 250 %. On the other hand, no significant effect of UV irradiation on THM concentrations was observed by [23] (LPUV and MPUV lamps) and by Vrillet [24] (LPUV lamps). It is difficult to explain the discrepancy between the conclusions of these studies because many factors can affect the production of THMs such

as the pool attendance, hydraulic residence time, UV dose, UV wavelength, free chlorine concentration and loss of volatile DBPs by stripping.

In order to better understand the effects of UV dechloramination on the formation of DBPs, laboratory experiments have been carried out in the present study under fully controlled conditions. Four pool water samples were exposed to UV light in a photoreactor equipped with a LPUV lamp in the presence of free chlorine ($[\text{Free chlorine}]_0$ = 3 mg L^{-1}) and at UV doses up to 47 kJ m^{-2} which correspond to typical cumulative UV doses received by real swimming pool waters for residence times ranging from 5 to 10 days. After exposure to UV light, pool water samples were post-chlorinated ($[\text{Free chlorine}]_0$ = 3 mg L^{-1}). The effects of UV doses on the chlorine demands and on the formation of DBPs during the post-chlorination treatment have been investigated.

2. Materials and Methods

2.1. Preparation of solutions

All solutions were prepared from reagent-grade chemicals and purified water delivered by a Millipore system (Milli-RX75/Synergy 1985). The stock solution of sodium hypochlorite (≈ 3 g Cl_2 L^{-1}) was prepared in purified water by dilution of a commercial solution of sodium hypochlorite (13% Acros Organics) and addition of hydrochloric acid to adjust the pH to about 8.5-9.0 and then stored in the dark at 4°C. Free chlorine concentration in the stock solution was determined just before use by iodometric titration.

Dilute solutions of free chlorine (3 mg Cl_2 L^{-1}) were prepared in phosphate buffered water ([TOC] ≤ 0.1 mg C L^{-1}, pH = 7.4) and in tap water of the city of Poitiers ([TOC] = 0.4 mg C L^{-1}, pH = 7.4) in order to compare the photodecomposition rates of free chlorine in various types of water.

2.2. Pool water samples

Four water samples were collected from three public indoor swimming pools between 8.00 am and 9.00 am, and used immediately upon arrival at the laboratory (Table 1). All the pools were treated by chlorine gas or sodium hypochlorite and none of them had a UV dechloramination system. Water samples were collected into a 10-L glass bottle. After collection, free and combined chlorine were not quenched by a reducing agent because the time elapsed between sampling and the arrival of the samples at the laboratory did not exceed 30 min. The concentrations of free and total chlorine, total organic carbon (TOC) and nitrate, the pH and the UV absorbance at 254 nm of the four pool water samples have been reported in Table 1.

2.3. UV photoreactor

Photolysis experiments were conducted by using a thermostated cylindrical batch reactor (Fig. S1 in the Supplementary Material). All experiments were performed at 25.0 ± 0.5 °C. The reactor was equipped with a LPUV lamp (Vilber Lourmat, 6 W) emitting at 254 nm. The UV lamp was turned-on during at least 20 min in a separated reactor in order to stabilize light output before introducing the lamp into the photoreactor. The volume of the aqueous solution in the reactor (V) and the annular path length of the reactor (l) were equal to 4.00 L and 6.25 cm, respectively. The photonic flux emitted by the UV lamp (I_0) was determined from photodecomposition rates of hydrogen peroxide as described previously by Nicole et al. [25]. The mean value of (I_0) was found to be equal to (4.52 ± 0.13) 10^{-6} E s^{-1} (Table S2) and corresponds to an irradiance of 19.5 J s^{-1} m^{-2}. The UV dose and the wavelength of the photoreacteor were chosen to be representative of the dechloramination process using low-pressure UV lamp, commonly used in indoor swimming pool water.

2.4. Experimental procedures

Immediately upon the arrival of the pool water sample at the laboratory, a fraction of water was transferred into a 5000-mL volumetric flask. The concentration of free chlorine was then determined by

the N,N-diethyl-p-phenylene diamine (DPD) colorimetric method and adjusted to 3 mg Cl_2 L^{-1} ($[Cl_2]_0$ = 3 mg L^{-1}) by adding the appropriate volume of the stock solution of sodium hypochlorite under mixing. The chlorinated water sample was allowed to stand for 2 min under mixing in order to homogenise the solution. The concentrations of free and of combined chlorine were then determined again by the DPD colorimetric method.

In a first series of experiments, a volume of 4 L of chlorinated pool water sample was introduced in the photoreactor and exposed to UV light for reaction times ranging from 15 to 30 min. At various irradiation times, free and total chlorine were determined by the DPD colorimetric method. In the case of a pool water sample (0410BLA), 10 mL samples of water were withdrawn from the UV reactor and transferred into 20 mL glass vials. The total sampled volume during the experiment does not exceed 200 mL, thus the total volume of the reactor was considered constant. The concentration of free chlorine in each vial was adjusted to 3 mg Cl_2 L^{-1}. All vials were then sealed with Teflon-lined caps and stored in the dark at 25.0 °C for 24 h.

In a second series of experiments, a volume of 4 L of chlorinated pool water sample was introduced in the photoreactor and exposed to UV light for two consecutive periods of 20 min corresponding to UV doses of 23.5 and 47 kJ m^{-2} (Fig. 1). A volume of 250 mL of chlorinated water was also transferred (control) in a well sealed glass bottle leaving no head space and stored in darkness at 25.0 °C for 24 h. At the end of each period of UV exposure of 20 min, the UV lamp was removed from the reactor (end of the first period) or turned off (end of the second period) and the remaining concentration of free chlorine in the UV reactor was immediately determined by the DPD colorimetric method and then adjusted to 3.0 mg Cl_2 L^{-1}. After 2 min of mixing in the UV reactor, 250 mL samples were withdrawn from the reactor. The two chlorinated samples of 250 mL were immediately transferred after sampling into well sealed glass bottles leaving no head space and stored in darkness at 25.0 °C for 24 h.

After a post-chlorination time of 24 h, the remaining concentrations of free chlorine in the vials or in the bottles were determined in order to determine the chlorine demands of the water samples during the post-chlorination step. The reactions of chlorine with organic and inorganic species were then stopped by adding 0.25 µL of sodium thiosulfate (1 M) and 0.5 µL of HCl (2 M) per mL of water sample. The water samples present in the bottles were transferred in 125 mL amber bottles with no head space for storage in the dark at 4°C prior to DBP analyses. All the analyses of DBPs were made within a storage time of 5 days.

2.5. Analytical methods

2.5.1. Analyses of organohalogenated by-products

THMs were analyzed by the headspace technique combined with GC-MS. HANs, CH, DCP, TCP and TCNM were determined after liquid-liquid extraction by GC according to the USEPA Method 551.1. Haloacetic acids (HAAs) were determined according to the USEPA Method 552.2. The analytical protocols, the detection and quantification limits for each DBP have been reported in the Supplementary Material (Section S2.3).

The concentration of adsorbable organic halide (AOX) was determined according to the NF EN 1485 method by using a DX-20 Dohrmann AOX analyser. Analyses of AOX were made in duplicate and the relative standard deviation was 10 %.

2.5.2. Other analytical methods

Free chlorine concentration in the stock solution of sodium hypochlorite was determined by iodometry. Free and combined chlorine concentrations in swimming pools were determined by the DPD colorimetric with a portable spectrophotometer (Palintest 7500) using 10 mL of water samples and commercial DPD1 and DPD3 tablets.

The total organic carbon (TOC) was determined by a Shimadzu TOC analyzer (TOC-V_{CSH}).

Chlorate was determined by ion chromatography (Dionex 4000) equipped with a column (AS-19), an electrochemical suppressor (ASR-4mm) and a conductimetric detector. Sodium hydroxide (10 mM) was used as eluent (flow rate of 1 mL min^{-1}). The injection volume was 500 µL adopted. The detection and quantification limits were 30 and 100 $\mu g.L^{-1}$, respectively.

3. Results

3.1. Photodecomposition of free and combined chlorine

Fig 2a shows that the rates of decomposition of free chlorine ($[Free\ chlorine]_0$ = 3.0 mg Cl_2 L^{-1}) in phosphate buffered ultra-pure water (pH = 7.4; TOC ≈ 0.1 mg C L^{-1}) and in tap water of the city of Poitiers (pH = 7.2; TOC = 0.40 ± 0.05 mg C L^{-1}) were identical and first-order with respect to free chlorine (Fig. 2b). The apparent quantum yield of photodecomposition of free chlorine at 254 nm ($\Phi_{Free\ chlorine}$) and at neutral pH, determined from the first-order rate constant of photodecomposition of free chlorine (k_{app} = 1.06 10^{-3} s^{-1}) and by using an apparent molar coefficient absorption of 62.5 M^{-1} cm^{-1} for free chlorine at pH 7.2-7.4 was found to be equal to 1.06 (Section S.3.1). This value confirms the values determined by Feng et al. [14].

The data obtained with the two pool water samples ($[Free\ chlorine]_0$ = 3 mg L^{-1}; $[Combined\ chlorine]_0$ = 0.7-0.8 mg L^{-1}; [TOC] = 5.5-5.6 mg L^{-1}; pH = 7.4-7.6) demonstrate that the decomposition rates of free chlorine were faster in pool water than in pure water (Fig. 2a) and did not follow a simple first-order kinetics (Fig. 2b). These data are consistent with published works which showed that organic solutes can significantly promote the photodecomposition of free chlorine [14, 26]. The data also indicate that free chlorine was almost completely removed after an irradiation time of 20 minutes corresponding to a UV dose of 23.5 kJ m^{-2} (Fig. 2a) and that the photodecomposition rates of combined chlorine in the pool water were equal or lower than the decomposition rates of free chlorine (Table 1). In full scale installations, the removal of chlorine species (as determined by DPD) between the inlet

and the outlet of the UV reactor is usually low (a few %) but the removals during one day of treatment or during the residence time of water in the pool is not negligible because the water is continuously recirculated in the UV reactor. The data concerning the decay of combined chlorine will not be discussed here because the DPD colorimetric method used in this work is not an appropriate analytical method for the quantification of the various inorganic and organic chloramines present in the pool water samples.

3.2. Production of chlorate

Ionic chromatography (IC) analyses showed that significant concentrations of chlorate ion (between 3.3 and 4 mg L^{-1}) were found in swimming pools disinfected by sodium hypochlorite (Table 1). These data can be attributed to the presence of chlorate in the commercial solutions of NaOCl because chlorate is formed by hydrolysis of hypochlorite during the storage of NaOCl solutions. IC analyses also demonstrated that the photodecomposition of free chlorine in ultra-pure water (phosphate buffer: pH = 7.4; $[Chlorine]_0$ = 55 µM) leads only to the production of chloride and chlorate ions as stable photo-products. As shown in Fig. S4, the production of chlorate in ultra-pure water was approximately 0.09 mole of chlorate/mole of chlorine photodecomposed (≈ 0.13 mg ClO_3^- formed/mg Cl_2 decomposed), in agreement with our previous works [27]. Yields ranging from 0.05 to 0.11 mol ClO_3^-/mol Cl_2 decomposed were obtained from experiments performed with tap water and with pool water samples (Table 2). Chlorate ion is formed by secondary reactions involving primary photoproducts of HOCl and ClO^- (hydroxyl radicals, chlorine and oxygen atoms, …) but the reaction pathways have not yet been elucidated.

3.3. Effect of the UV treatment on the chlorine demand during the postchlorination step

Without UV pre-treatment, the chlorine demands of the four pool water samples during the post-chlorination step ($[Free\ chlorine]_0$ = 3 mg Cl_2 L^{-1}, Contact time = 24 h, 25°C) ranged between 0.2 and

1.4 mg Cl_2 L^{-1} or between 0.07 and 0.28 mg Cl_2/mg TOC. The large difference in the chlorine consumptions can be attributed to the differences in the concentrations and in the nature of chlorine-consuming species that remain in pool water (organic solutes, nitrogen species, chloramines). It should be noted that a chlorine demand of 0.2 mg L^{-1} represents an abnormally low value.

Data obtained with the pool water sample 0410BLA (Fig. 3a) showed that UV irradiation led to an increase in the chlorine demand of pool water during the post-chlorination step. The chlorine demand increased from 1.45 mg Cl_2 L^{-1} (0.26 mg Cl_2/mg TOC) for the control sample (UV dose = 0 kJ m^{-2}) to approximately 2.5-2.7 mg Cl_2 L^{-1} (0.45-0.50 mg Cl_2/mg TOC) for UV doses of 23-35 kJ m^{-2} (irradiation time = 20-30 min). It should be noted that the amounts of chlorine decomposed during the UV treatment (Fig. 2a, 3 mg Cl_2 L^{-1} after 20 min of UV irradiation) have not been taken into account in the chlorine demand and that a residual of free chlorine was present in all the pool water samples after a post-chlorination time of 24 h.

The increase in the chlorine demand after UV treatment has also been confirmed by experiments performed with the four pool water samples at UV doses of 23.5 and 47 kJ m^{-2} according to the experimental conditions described in Fig. 1. The percentages of increase in the chlorine demand were approximately equal to 50-70 % for 0410BLA; 150- 220 % for 0427GAN and 0428BEL and about 520-620 % for 0421GAN (Table 2 and Fig. 4a). The latter value is very high because of the abnormal low value of the chlorine demand of the control sample (0.2 mg Cl_2 L^{-1}). These data demonstrate that UV dechloramination of swimming pool waters leads to the formation of by-products which are more reactive with chlorine than the parent compounds, most probably via secondary reactions involving photo-products generated from the photolysis of chloramines and free chlorine. Our data also demonstrate that UV dechloramination of swimming pool water would increase the chlorine consumption by two main ways: direct photolysis reactions of free chlorine in the UV chamber and increase in the chlorine demand of the pool water.

3.4. Effect of UV dechloramination on the post-chlorination DBP formation

For the pool water sample 0410BLA, Fig. 3 presents the effects of UV doses (in the range 0-35 kJ m^{-2}) on the concentrations of chloroform (TCM) (Fig.3a), TCP and TCNM (Fig.3b) measured after the post-chlorination treatment. For the four water samples, Table 2 and Fig.4b-4d) show the concentrations of DBPs obtained from experiments which have been carried out under the conditions described in Fig. 1 (UV doses : 0, 23.5 and 47 kJ m^{-2}). It must be emphasized that UV exposure has been performed in the presence of free chlorine and that the total amounts of free chlorine decomposed in the UV reactor are equal to 3 and 6 mg L^{-1} for UV doses of 23.5 and 47 kJ m^{-2}, respectively. The effects of UV treatment will be discussed below by examining the effects of UV doses on the concentrations of DBPs or on the $[C]_{23.5}$:$[C]_0$ or $[C]_{47}$:$[C]_0$ ratios, where $[C]_0$ represents the concentration of a DBP or of a group of DBPs in the control sample (non-irradiated sample, UV dose = 0 kJ m^{-2}) and $[C]_{23.5}$ and $[C]_{47}$, the concentrations in samples which have been exposed to UV doses of 23.5 and 47 kJ m^{-2}, respectively.

3.4.1. Effect of UV dechloramination on the formation of AOX

Concentrations of AOX in the four control water samples (UV dose: 0 kJ m^{-2}) determined after the post-chlorination step ranged from 510 to 1110 µg L^{-1} (Table 2) and the highest concentrations of AOX were found in pool waters having the highest TOC content. The concentration levels of AOX obtained with the four studied samples were consistent with published values (Brunet et al., 2010). As it will be detailed later in the manuscript, the monitored BDPs (THMs HANs, CH, DCP, TCP, TCNM and HAAs) represent approximatively 50 % of the AOX . This is consistent with previously published data where the unidentified AOX represents more than 60 % of the AOX in drinking water [28].

Data in Table 2 show that the UV treatment (UV dose = 47 kJ m^{-2}) in the presence of free chlorine increased the post-chlorination AOX formation by approximately 20 % (Table 2; $1.13 < [AOX]_{47}:[AOX]_0 < 1.29$). AOX analyses have not been done for the UV dose of 23.5 kJ m^{-2}. The

increase in the AOX formation after UV exposure is also consistent with the data obtained for the chlorine demand because an increase in the AOX formation can be expected when the chlorine demand increases.

3.4.2. Effect on the formation of THMs

GC/MS analyses of pool water samples showed that the total concentration of THMs (TTHMs) ranged from 29 to 69 µg L^{-1} and accounted for 5.5 % (sd = 0.5, 4 values) of the AOX concentration of the studied waters (Table 2). TCM was the dominant THM and represented 85-90 % of the TTHMs. The contribution of bromodichoromethane (BDCM) and dibromochloromethane (DBCM) to the TTHMs were approximately 10 and 2.5%, respectively. Concentrations levels of bromoform (TBM) were very low (0.4-1 µg L^{-1}). It should also be noted that a comparison of THM concentrations determined before and after post-chlorination of the control samples indicates that the post-chlorination treatment did not increase the concentrations of THMs by more than 10 % (data not shown).

Data presented in Fig. 3a show that UV irradiation of the pool water 0410BLA in the presence of free chlorine increased the TCM formation during the post-chlorination step by approximately 80 %. Interestingly, the post-chlorination TCM formation did not significantly increase for pre-irradiation doses higher than 12 kJ m^{-2}, which corresponds to an irradiation time of 10 min and to a 75% decomposition of free chlorine in the UV reactor (Fig. 2a). These data suggest that the effect of UV radiation on the formation of TCM might be mainly attributed to reactions between the organic solutes present in pool water and the transient species generated from the photolysis of free chlorine and chloramines.

These data were confirmed by the experiments carried out with the four water samples under the conditions described in Fig. 1. As shown the data reported in Table 2 and in Fig. 4b, UV doses of 23.5 ad 47 kJ m^{-2} increased the post-chlorination chloroform formation by approximately 90 % (mean value for $[TCM]_{23.5}$:$[TCM]_0$ = 1.94, sd = 0.40) and 150 % (mean value for $[TCM]_{47}$:$[TCM]_0$ = 2.53, sd =

0.75), respectively. As depicted in Fig. 4b, the mean increase in the chloroform formation was higher for the first irradiation dose of 23.5 kJ m^{-2} (mean value for $[TCM]_{23.5}/[TCM]_0$ = 1.94, sd = 0.40) than for the second irradiation of 23.5 kJ m^{-2} (mean value for $[TCM]_{47}$:$[TCM]_{23.5}$ = 1.29, sd = 0.11). Since TCM represents the dominant THM (≈ 85 % of TTHMs), UV treatment also increased the post-chlorination formation of TTHMs by 84 % and 165 % for UV doses of 23.5 and 47 kJ m^{-2}, respectively (mean value for $[TTHMs]_{23.5}$:$[TTHMs]_0$ = 2.04, sd = 0.44; $[TTHMs]_{47}/[TTHMs]_0$ = 2.65, sd = 0.76). UV treatment also markedly increased the concentrations of BDCM ($[BDCM]_{23.5}$:$[BDCM]_0$ = 3.21, sd = 0.82; ($[BDCM]_{47}$:$[BDCM]_0$ = 4.17, sd = 1.22) and DBCM ($[DBCM]_{23.5}$:$[DBCM]_0$ = 2.16, sd = 0.46; ($[DBCM]_{47}$:$[DBCM]_0$ = 2.29, sd = 0.34). The increases in the concentrations of BDCM and DBCM were higher that than those obtained for TCM but the concentrations levels of BDCM and DBCM are much lower that the concentrations of TCM. On the contrary, the UV treatment reduced the formation of TBM. These data can be explained by the fact that brominated THMs can be photodecomposed by UV light emitted by LPUV lamps (molar absorption coefficient (ε) of TCM, BDCM, DBCM and TBM at 254 nm : < 0.1 , 42.3, 228.5 and 519 M^{-1} cm^{-1}, respectively; quantum yield (Φ) at 254 nm = 0.43 for BDCM, DBCM and TBM, [29]). By using the values of ε and Φ, calculations indicate that the percent removals of BDCM, DBCM and TBM at a UV dose of 23.5 kJ m^{-2} should be roughly equal to 30, 85 and 98 %, respectively. These calculations can be used to explain the decrease in the concentration of TBM in UV treated waters. In the case of BDCM, DBCM, the observed increase in the concentrations of these two THMs in post-chlorinated water suggest that the amounts of BDCM and DBCM formed during post-chlorination were higher than the amounts of BDCM and DBCM which were photodecomposed in the UV reactor. In their full-scale study of the effect of UV-dechloramination on the formation of THM, Cassan et al. [22] observed an increase in the concentration of TCM and of BDCM and a decrease in the concentrations of DBCM and TBM in water when the MPUV lamp was

turned on. As compared to LPUV lamps, MPUV lamps are more efficient for the photodegradation of brominated THMs because these DBPs have a broad absorption band with a maximum at 220 nm [29].

It should also be noted that the contribution of TTHMs to AOX increased from 5.5 % (sd = 0.5, 4 values) to ≈ 12.2 % (sd = 4.3, 4 values) when the UV dose increased from 0 to 47 kJ m^{-2}.

3.4.3. Effect on the formation of HAAs

For the control samples (UV dose = 0 kJ m^{-2}), the total concentration of HAAs including the five HAAs measured in the present work (monochloroacetic acid (MCAA); dichloroacetic (DCAA); trichloroacetic acid (TCAA); bromochloroacetic acid (BCAA) and dibromoacetic acid (DBAA)) ranged from 208 to 530 µg L^{-1} and represented 24.6 % (sd = 2.3, 4 values) of the AOX (Table 2). Among the HAAs, DCAA (117-361 µg L^{-1}; 58% of total HAAs) and TCAA (74-183 µg L^{-1}, 37% of total HAAs) were the two dominant HAAs and accounted for 93.5-96 % of the total HAAs. MCAA and BCAA were detected at concentration levels ranging from 6 to 15 µg L^{-1} and the concentrations of DBAA were below the quantification limit of 1 µg L^{-1}.

As shown the data in Table 2, the UV dechloramination pre-treatment of the four pool water samples did not affect the speciation of HAAs and the total concentration of HAAs in post-chlorinated samples because the variations in the concentrations of HAAs were within the analytical errors ($[THAAs]_{23.5}$:$[THAAs]_0$ = 1.04, sd = 0.04; $[THAAs]_{47}$:$[THAAs]_0$ = 0.99, sd = 0.13).

3.4.4. Effect on the formation of chloral hydrate (CH)

In agreement with published works [6, 30], CH was one of the most abundant DBP in swimming pool waters. Concentration levels of CH in control samples varied from 100 to 380 µg L^{-1} and represented approximately 17.9 % (sd 5.5; 4 values) of the AOX (Table 2). Data in Table 2 and in Fig. 4c show that the UV dechloramination treatment leads to a relative small increase in the post-chlorination formation of CH ($[CH]_{23.5}$:$[CH]_0$ = 1.18, sd = 0.16; $[CH]_{47}$:$[CH]_0$ = 1.27, sd = 0.22).

3.4.5. Effect on the formation of haloacetonitriles (HANs)

With regards to HANs, analyses of dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN) in control samples showed that the concentration levels of DCAN and of CBAN ranged from 2.8 to 18.6 µg L^{-1} and from 0.8 to 3.8 µg L^{-1}, respectively (Table 2). DCAN accounted for 75% to total HANs (sd = 7.5; 4 values) and BCAN for 21 % (sd = 4.2; 4 values). TCAN and DBAN were not detected in all samples and their concentrations were always less than 1 µg L^{-1}. When the water samples were exposed to UV radiation, significant increases in the concentrations of DCAN ($[DCAN]_{23.5}$:$[DCAN]_0$ = 2.19, sd = 0.56; $[DCAN]_{47}$:$[DCAN]_0$ = 2.73, sd = 1.05) and of ($[BCAN]_{23.5}$:$[BCAN]_0$ = 2.28, sd = 0.67; $[BCAN]_{47}$:$[BCAN]_0$ = 2.66, sd = 0.80) were observed after the post-chlorination step (Table 2 and Fig. 4d).

3.4.6. Effects on the formation of 1,1-dichloropropanone (DCP) and 1,1,1-trichloropropanone (TCP)

DCP was detected in only one control sample at a concentration of 3.2 µg L^{-1} and in post-chlorinated water samples at concentrations less than 0.3 µg L^{-1} (Table 2). Data obtained for TCP demonstrate that the concentration of TCP in the four control samples ranged from 0 to 11.4 µg L^{-1} and that UV treatment significantly increased the concentrations of TCP in post-chlorinated samples (Table 2 Fig. 4d).

3.4.7. Effect on the formation of chloropicrin (TCNM)

TCNM was detected in two control water samples at concentrations of 0.4 and 1 µg L^{-1} (Table 2) which are of the same order of magnitude than values reported in literature [2]. As shown the data presented in Figs 3b and 4d and in Table 2, UV dechloramination / post-chlorination sequence significantly increased the TCNM formation to concentration levels ranging from 1.6 to 3.8 µg L^{-1}. For the two

control water samples which did not contain TCNM (detection limit: 0.1 µg L^{-1}), the concentrations of TCNM were approximately equal to 1.6-2.2 µg L^{-1}. For the two other pool waters, TCNM concentrations increased by up to 300-350 % after the UV dechloramination/post-chlorination treatment ($[TCNM]_{23.5}$:$[TCNM]_0$ = 8.60, sd = 6.61; $[TCNM]_{47}/[TCNM]_0$ = 9.52, sd = 9.09, 3 values). An increase in the formation of TCNM has also been previously observed with drinking water samples when chlorination followed a UV treatment with MPUV lamps in the absence of free and combined chlorine [31].

TCNM is a by-product resulting of the chlorination of nitro-organic compounds. However, the identity of TCNM precursors in drinking waters and in swimming pool waters is unknown. It has also been shown that pre-ozonation of natural water, drinking water or treated wastewater prior to chlorination can substantially increase the formation of TCNM [32-34] and of other halonitromethanes [35, 36] probably because ozonation facilitates the oxidation of nitrogen compounds into nitro-organic compounds. MPUV irradiation of drinking water prior to chlorination was also found to increase the TCNM formation whereas LPUV irradiation had no effect on TCNM formation [31]. Precursors of TCNM can also be formed from non-nitrogenous organic solutes by dark nitration reactions occurring during the oxidation of nitrite by various oxidants (chlorine, ozone, chlorine dioxide, monochloramine) in the presence of phenols [37] or by photonitration reactions occurring during UV irradiation of phenols in the presence of nitrate [38].

In the present work, UV irradiation of pool water samples has been performed with a LPUV lamp, high UV dose (up to 47 kJ m^{-2}) and in the presence of free chlorine ($[Free\ Cl_2]_0$ = 3 mg L^{-1}), combined chlorine ($[Combined\ Cl_2]_0$ = 0.3-0.8 mg L^{-1}) and nitrate (≈ 0.5-0.8 mM). The substantial increase in the formation of TCNM which has been observed after UV dechloramination and post-chlorination treatments can be attributed to various reactions which have already been proposed to explain the

effects of water treatment processes (ozonation, UV disinfection) or of nitrite ion on the formation of TCNM. Highly reactive hydroxyl radicals formed during photolysis of free chlorine [15, 20], nitrite and nitrate ions [39] can oxidise nitrogenous organic solutes into more reactive TCNM precursors. Nitrite ion formed by photolysis at 254 nm of monochloramine [16, 17] and nitrate [40] may also lead to the formation of nitro-compounds during its oxidation by free chlorine and other oxidizing species in the presence of organic solutes. In addition, photonitration reactions involving transient species formed during photolysis of nitrate, nitrite and chloramines may also be a source of TCNM precursors.

4. Conclusions

This laboratory-scale study demonstrates that UV dechloramination of swimming pool water by LPUV lamps and at UV doses similar to those usually applied for real pool water (cumulative UV doses up to 50 kJ m^{-2} and presence of free chlorine) significantly increases the chlorine demand of pool waters and the formation of some DBPs (more particularly TCM, BDCM, CDBM, DCAN, TCP and TCNM) during the post-chlorination step. All these data will be confirmed by our full-scale studies (not presented here) because similar trends were obtained for the effects of UV dechloramination by MP UV lamps on the chlorine consumption and on the formation of DBPs.

This study supports that UV dechloramination of swimming pool water significantly changes the formation potentials of DBPs because UV treatment initiate numerous oxidation, hydroxylation and nitration reactions involving transient species (Cl°, HO°, organic radicals…) formed from the photolysis of free chlorine species, chloramines and nitrate ions. As the precursors of the various DBPs in swimming pool water are not well known and because of the complexity of reaction pathways, additional research is needed in order to elucidate most of the reaction mechanisms, and in particular, the reaction pathways leading to the increase in the formation of THMs and of TCNM.

Acknowledgments: French Agency for Food, Environmental and Occupational Health & Safety (ANSES, Paris) for funding this study.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:

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List of Tables

Table 1 - Composition of the four swimming pool water samples and experimental data obtained for the photodecomposition rates of free and combined chlorine and for the molar yields of chlorate in swimming pool waters.

Swimming water sample	**Pure water**	**Tap water Poitiers**	**0410BLA**	**0421GAN**	**0427GAN**	**0428BEL**
Sampling date		April 10, 2010	April 10, 2010	April 21, 2010	April 27, 2010	April 28, 2010
Disinfectant used		Cl_2 gas	NaOCl	Cl_2 gas	Cl_2 gas	NaOCl
UV transmittance at 254 nm (cm^{-1})			98.6	98.7	98.8	98.7
Alkalinity (mg $CaCO_3$ L^{-1})			103	66	67	95
Nitrate (mg L^{-1})			46.3	38.0	34.2	39.9
Chlorate (mg L^{-1})	0	< 0.1	3.96	< 0.1	< 0.1	3.30
[Free Cl_2]/ [Total Cl_2] (mg L^{-1})[a]	0	<0.05/<0.05	1.08 / 1.94	2.45 / 2.8	2.9 / 3.2	2.2 / 2.85
pH	7.4	7.2	7.63	7.57	7.57	7.43
TOC (mg C L^{-1})	≤ 0.10	0.35	5.54	2.75	2.82	5.13
$[Free\ Cl_2]_0$ (mg Cl_2 L^{-1})[b]	3.0	3.0	3.0	3.0	2.9	2.8
$[Combined\ Cl_2]_0$ (mg Cl_2 L^{-1})[b]	0	0	0.7	0.4	0.3	0.8
Irradiation time for 50 % decay of free Cl_2 (min)	11.75	11.75	6.0	7.5	6.5	4.5
UV dose for 50 % decay of free Cl2 (kJ m^{-2})	12.5	12.5	7.0	8.8	7.6	5.3
Irradiation time for a 90 % decay of free Cl_2 (min)	35.5	35.5	17	16	15.5	11
UV dose for a 90 % decay of free Cl_2 (kJ m^{-2})	41.5	41.5	19.9	18.7	18.1	12.9
Irradiation time for 50 % decay of combined Cl_2 (min)	-	-	11	6.5	11	7
UV dose for a 50 % decay of combined Cl_2 (kJ m^{-2})	-	-	12.9	7.6	12.9	8.2
Chlorate yield (mol ClO_3^- formed/mol Cl_2 decomposed)	0.09	0.10	nd[c]	0.10	0.05	0.11

[a]Values measured immediately after the arrival of the samples in the laboratory

[b]Concentrations determined just before the beginning of the photolysis experiments.

[c]The concentration could not be determined accurately in this sample.

Table 2 – Effects of UV treatment (UV dose = 0, 23.5 or 47 kJ m^{-2}) on the chlorine demands and on the production of DBPs during the postchlorination step (Experimental conditions: see Fig. 1).

Pool water	**0410BLA**			**0421GAN**			**0427GAN**			**0428BEL**		
UV Dose (kJ m^{-2})	0	23.5	47	0	23.5	47	0	23.5	47	0	23.5	47
TOC (mg C L^{-1})	5.54			2.75			2.82			5.13		
Cl_2 demand mg Cl_2 L^{-1})	1.46	2.53	2.20	0.20	1.44	1.24	0.70	1.74	1.78	0.70	2.28	2.27
AOX (µg L^{-1})	1000		1290	510		580	500		580	1110		1320
Trihalomethanes (THMs)												
TCM (µg L^{-1})	54.5	85.2	100.7	31.8	70.2	94.9	24.7	58.3	82.7	61.4	99.6	120.3
BDCM (µg L^{-1})	6.8	14.9	17.5	3.6	13.4	18.4	3.2	12.8	16.5	5.4	15.7	20.6
DBCM (µg L^{-1})	1.6	2.6	3.3	0.9	1.8	1.8	0.8	2.1	2.0	1.2	2.9	3.2
TBM (µg L^{-1})	0.7	0.6	0.4	0.9	0.5	0.4	0.4			0.7	nd	nd
TTHM (µg L^{-1})	63.6	103.2	121.8	37.2	85.9	115.5	29.1	73.2	101.2	68.7	118.2	144.1
% TTHM in AOX	5.41		7.99	6.16		16.85	4.96		14.78	5.33		9.28
Haloacetic acids (HAAs)												
MCAA (µg L^{-1})	7.8	10.2	8.7	5.4	7.8	9.7	6.6	7.5	9.2	18.9	20.7	21.5
DCAA (µg L^{-1})	168.4	157.8	147.2	116.9	131.3	138.7	138.6	141.5	159.5	361	371.7	343.8
TAA (µg L^{-1})	183.2	187.3	143.8	80.41	78.1	81.5	73.6	70.9	75.5	135.8	138.9	122.4
BCAA (µg L^{-1})	8	5	7.3	6.0	6.5	6	7.9	3.7		15.5		8.6
DBAA (µg L^{-1})	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Total HAA (µg L^{-1})	367.4	360.3	307.0	208.4	223.7	235.9	226.7	223.6	244.2	531.2	531.3	496.3
% HAAs in AOX	21.8		14.0	23.75		23.3	26.0		24.2	27.1		21.2
Chloral hydrate (CH)												
CH (µg L^{-1})	363.4	367.0	399.4	107.6	140.8	154.2	99.6	131.7	146.7	378.1	403.7	400.3
% CH in AOX	23.4		19.9	13.6		17.1	12.8		16.3	21.9		19.5
Haloacetonitriles (HANs)												
DCAN (µg L^{-1})	18.6	29	28.9	3.4	8.3	11.9	2.8	7.9	10.4	7.1	13.7	15.2
BCAN (µg L^{-1})	3.8	5.6	6.4	0.8	2.3	2.8	1	2.8	3.1	2.4	4.7	5.7
DBAN (µg L^{-1})	0.55	0.4	0.24	0	0	0	0	0	0	0.6	0	0
TCAN (µg L^{-1})	0.06	0.06	0.08	0	0.1	0.1	0	0	0	0.8	0	0
Total HAN (µg L^{-1})	23.0	35.1	35.6	4.2	10.7	14.8	3.8	10.7	13.5	10.9	18.4	20.9
% HANs in AOX	1.44		1.73	0.52		1.60	0.47		1.45	0.61		0.98
Other DBPs												
DCP (µg L^{-1})	<0.1	<0.1	<0.1	<0.1	0.2	0.2	<0.1	<0.1	0.3	3.2	<0.1	<0.1
TCP (µg L^{-1})	1.5	9.1	6.2	1.0	6.9	13.8	< 0.3	5.5	9.1	11.4	22.4	28.6
TCNM (µg L^{-1})	0.4	2.6	1.9	<0.1	2.2	2.2	<0.1	1.6	2.0	1.0	3.3	3.8

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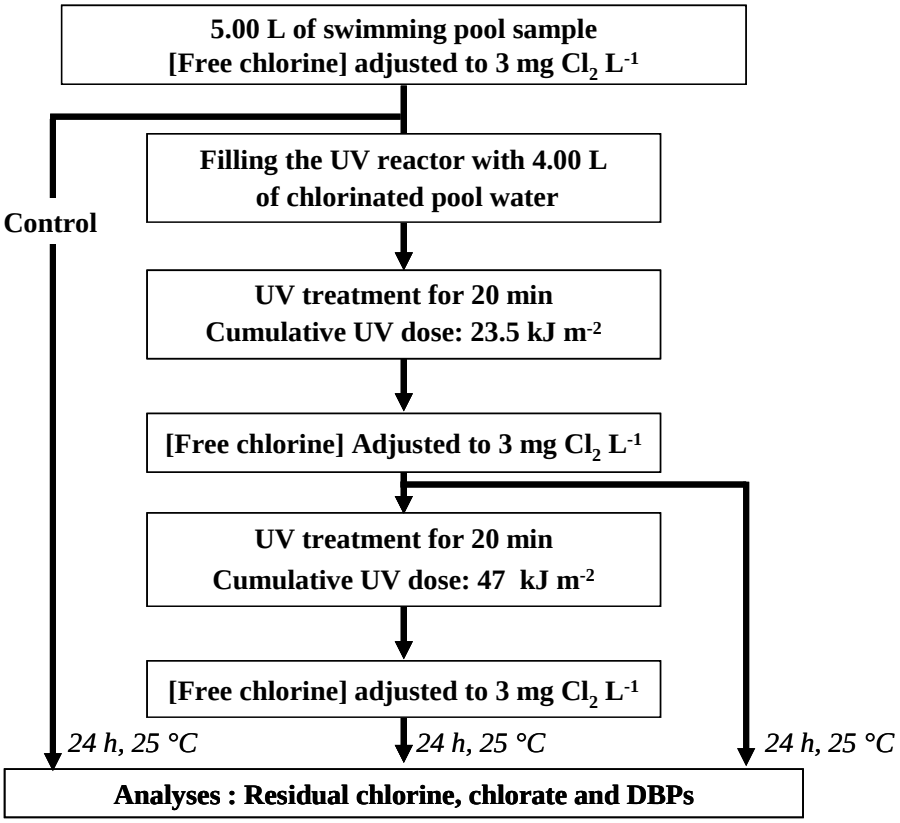


Fig. 1 - Experimental design for UV treatment and chlorination experiments.

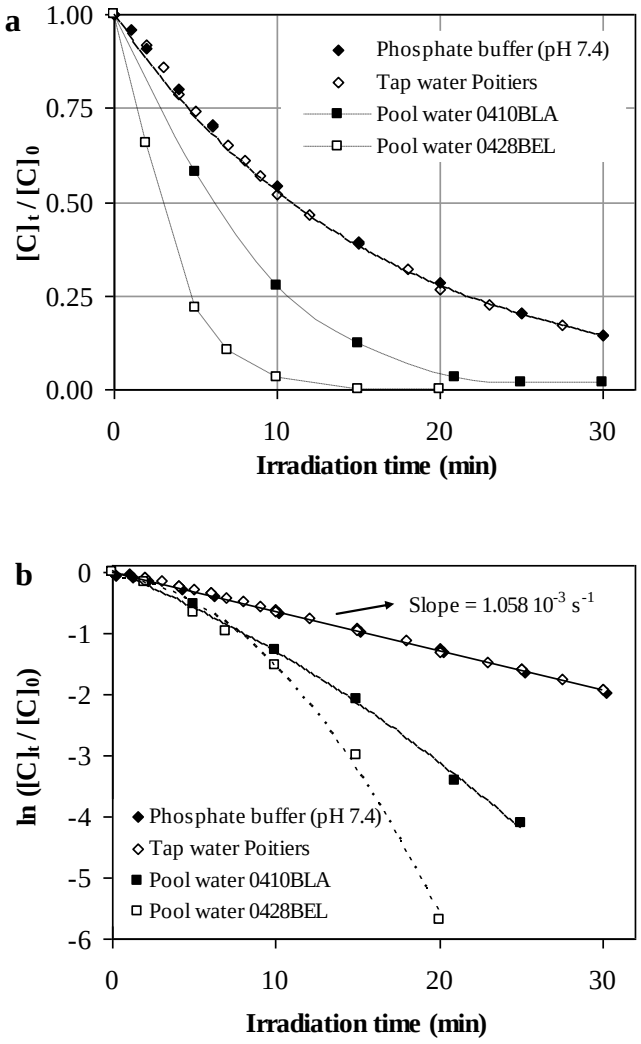


Fig. 2 - Photodecomposition of free chlorine in phosphate-buffered water, tap water and in two pool water samples. a) Concentration time profiles for free chlorine and b): first-order plots for free chlorine decomposition. ([Free chlorine]$_0$ = 3.0 mg L^{-1} = 42 µM; 25.0 °C; Irradiance = 19.5 W m^{-2}).

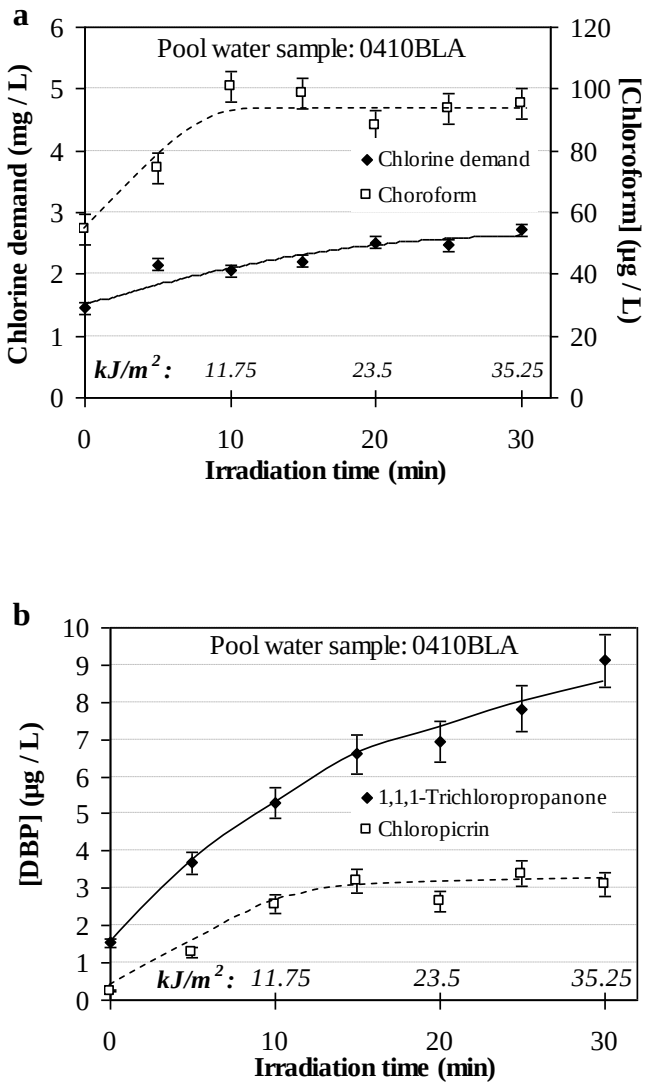
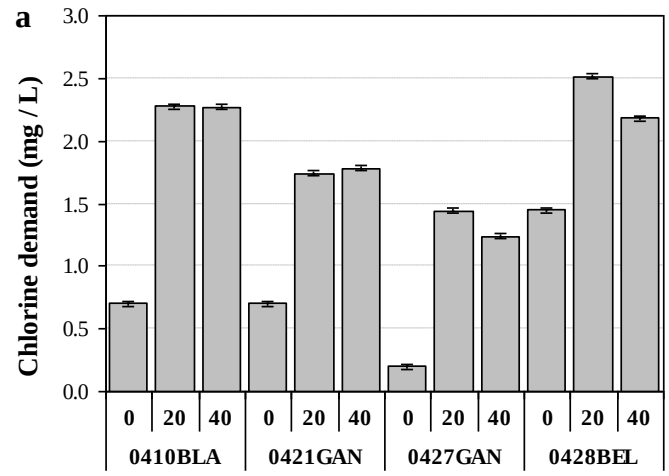


Fig. 3 - Effects of "UV + Cl_2" pre-treatment ($[Cl_2]_0$ = 3 mg L^{-1}; Irradiance = 19.5 W m^{-2}) on the chlorine demand of a pool water during post-chlorination (Fig. 3a) and on the concentrations of chloroform (Fig 3a) 1,1,1-trichloropropanone and chloropicrin (Fig. 3b) determined after the post-chlorination treatment (Post-chlorination: $[Cl_2]_0$ = 3 mg L^{-1}, Reaction time = 24 h, 25.0 °C).


a
Chlorine demand (mg / L)
3.0
2.5
2.0
1.5
1.0
0.5
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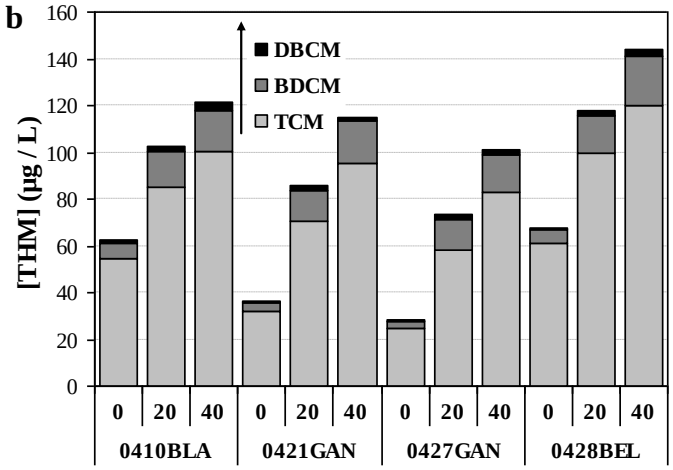
0 20 40 0 20 40 0 20 40 0 20 40
0410BLA
0421GAN
0427GAN
0428BEL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[THM] (µg / L)
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140
120
100
80
60
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20
0
DBCM
BDCM
TCM
0 20 40 0 20 40 0 20 40 0 20 40
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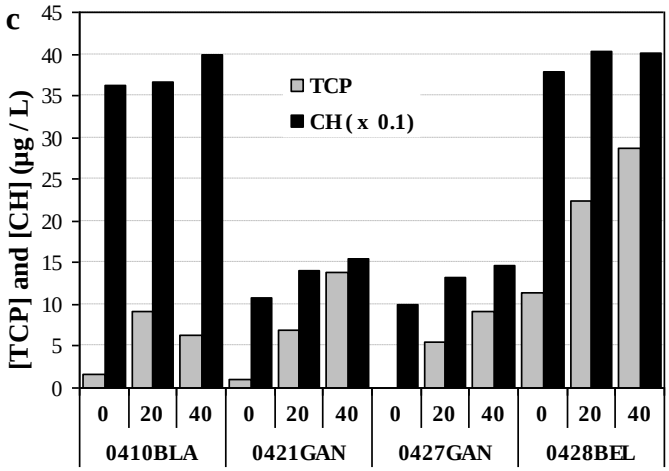
0421GAN
0427GAN
0428BEL


c
[TCP] and [CH] (µg / L)
45
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30
25
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15
10
5
0
TCP
CH (x 0.1)
0 20 40 0 20 40 0 20 40 0 20 40
0410BLA
0421GAN
0427GAN
0428BEL

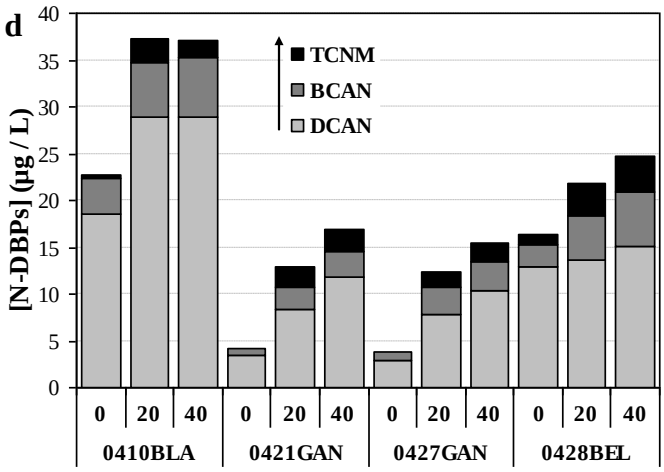

Fig. 4 - Effects of the "UV+ Cl_2" pre-treatment of four pool water samples on the chlorine demands (a) and on the concentrations of DBPs (b-d) determined after the post-chlorination treatment (UV exposure times of 0, 20 and 40 min corresponding to UV doses of 0, 23.5 and 47 kJ m^{-2}, respectively).